

On the Subsystem Formulation of Linear Response Time-Dependent DFT

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Abstract

The subsystem formulation of linear response time-dependent DFT (TD-DFT) is analyzed in detail. Two equivalent derivations are presented and naturally yield self consistent subsystem TD-DFT equations. One derivation is equivalent to the subsystem TD-DFT formalism of Neugebauer [J. Neugebauer, *J. Chem. Phys.* **126**, 134116 (2007)]. The other derivation yields Dyson type equations involving three types of subsystem response functions: coupled, uncoupled and Kohn–Sham.

Analysis of the pole structure of the subsystem response functions shows that a single subsystem response function contains information about the electronic spectrum of the entire supersystem. Comparison of the subsystem and supersystem response functions shows that, while the correlated response is subsystem additive, the Kohn–Sham response is not. This particularly puzzling aspect of the theory is found to be an artifact stemming from the subjective nature of the density partitioning in subsystem DFT. This aspect is analyzed and compared to the less subjective partition DFT theory.

This work sets the stage for a number of theoretical advances, such as the development of quasiparticle GW corrections to subsystem DFT, the development of a mapping between subsystem and supersystem Kohn–Sham orbitals, and the evaluation of non-local correlation energy with the adiabatic connection fluctuation dissipation theorem.

1 Introduction

When modeling systems that contain a large number of electrons, even the Kohn–Sham Density Functional Theory (KS-DFT) approach [1] has its limits. In the past decade many approximations, such the Fast Multiple Method of Scuseria [2] or methods exploiting the locality of chemical bonds [3], as well as the so-called real-space methods [4] made it possible to massively reduce KS-DFT complexity for spatially extended molecules. However, the large pre-factor of such scaling laws left the calculation of most realistic, fully-solvated systems still prohibitive [5, 6]. Despite the relatively favourable computational scaling of KS-DFT with the system size, most of KS-DFT simulations are bound to consider only small portions of the larger and more realistic system.

Reducing the computational complexity of KS-DFT by partitioning the total electron density of a system into subsystem contributions has been an appealing idea since the early works of Gordon and Kim [7, 8]. However, the success of KS-DFT seemed to have rendered partitioning methods unnecessary. This is evident from the Quantum Chemistry literature of the 70s and 80s, where partitioning methods were frequent only to high-end wave function methods, and interactions between subsystems were treated with various types of perturbation theory [9]. Despite two successful applications of density partitioning techniques, first by Senatore and Subbaswamy [10], and then by Cortona [11], revival of density partitioning methods is due to a paper by Wesolowski and Warshel published in 1993 [12]. Presently, subsystem DFT is being developed by many research groups worldwide [13–21]. Successful applications of subsystem DFT are reported for applications related to the ground state, such as analysis of electron densities [22], and spin densities [23]; and for calculations of charge and excitation energy transfer parameters [15, 24, 25]; as well as for electronic spectra and molecular prop-

erties [20, 26–30].

The time-dependent extension of subsystem DFT has been pioneered by Casida and Wesolowski [31]. However, Neugebauer [32] is credited for deriving working equations for the solution of the subsystem time-dependent DFT (subsystem TD-DFT, hereafter) and for applying subsystem TD-DFT to determine excitation energies [20, 28, 32], charge/exciton couplings [15, 24, 25], and molecular properties [33]. Similarly to subsystem DFT, subsystem TD-DFT is developed to take full advantage of the subsystem nature of the majority of real life systems. Solvated systems are a typical example of this. An early success story of subsystem TD-DFT is the calculation of solvatochromic shifts [34]. More recently, the electronic spectra of light harvesting complexes model systems containing more than 1000 atoms has been calculated with subsystem TD-DFT [28].

Such a large body of work on subsystem DFT and TD-DFT shows their usefulness and importance. Therefore, rather than focussing on proving that subsystem TD-DFT is a valuable alternative to regular TD-DFT of the supersystem, this work aims at clarifying the relationship between the subsystem and regular TD-DFT of the supersystem. Specifically, two questions are answered: (1) How does the KS and interacting response functions of the supersystem relate to the KS and interacting response functions of the subsystems? And (2) How do practical subsystem TD-DFT schemes compare to the exact theory?

Once a relationship between the subsystem formulation and the TD-DFT of the supersystem is clarified and exemplified by rigorous equations, a number of important advances of subsystem DFT will become available. For example, it will be possible to apply subsystem TD-DFT to compute non-local correlation energy with the adiabatic connection fluctuation dissipation theorem [35, 36], and to develop quasiparticle perturbative corrections to subsystem DFT, similarly to what done by the GW approximation for regular

KS-DFT [37].

In this work, a simple and general formalism of subsystem TD-DFT is derived, including equations needed for practical calculations involving perturbative solutions. The new derivations will be amenable to a deeper analysis and understanding of the theory of subsystem TD-DFT. In addition, relation with the TD-DFT of the supersystem will be established and analyzed. Dyson type equations for subsystem TD-DFT are sought and are used to determine how approximate treatments compare with the exact formalism.

This work is organized as follows. In the next section, a theoretical background is given on KS-DFT, subsystem DFT, and linear response TD-DFT. In Section 3, a rigorous derivation of linear response subsystem TD-DFT is carried out. In Section 4 an alternative derivation of subsystem TD-DFT is presented in terms of subsystem response functions. Section 5 is devoted to the comparison of subsystem TD-DFT with TD-DFT of the supersystem. In Section 6, conclusions and future directions are drawn.

2 Theoretical Background

2.1 Ground state DFT and subsystem DFT

KS-DFT can be summarized by the following equation, known as the KS equation, in canonical form,

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \phi_k(\mathbf{r}) = \varepsilon_k \phi_k(\mathbf{r}), \quad (1)$$

where v_{eff} is the effective potential that the one-particle KS orbitals, ϕ_k , experience, and ε_k are the KS orbital energies. The spin labels have been omitted for sake of clarity, as throughout this work only the spin restricted case is considered without loss of generality of the derivations. The electron density is simply $\rho(\mathbf{r}) = 2 \sum_i^{\text{occ}} |\phi_i(\mathbf{r})|^2$.

The effective potential, v_{eff} , is given by

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{eN}}(\mathbf{r}) + v_{\text{Coul}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}), \quad (2)$$

with v_{ext} being an externally applied time-independent potential, v_{eN} the electron–nucleus attraction potential, v_{Coul} the Hartree potential, and v_{xc} the exchange–correlation (XC) potential. Usually [1], v_{eN} is part of v_{ext} as they are both density independent. However, for sake of a consistent presentation of the following derivations, the two potentials are kept separated.

Subsystem DFT is based on the idea that an electronic (molecular) system can be more easily approached if it is partitioned into many smaller subsystems. In mathematical terms, this is done by partitioning the electron density as follows [10, 11]

$$\rho(\mathbf{r}) = \sum_I^{N_S} \rho_I(\mathbf{r}), \quad (3)$$

with N_S being the total number of subsystems. Self consistent solution of the following coupled KS-like equations (also called KS equations with constrained electron density [38]) yield the single subsystem KS orbitals, i.e.

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}^I(\mathbf{r}) \right] \phi_k^I(\mathbf{r}) = \varepsilon_k^I \phi_k^I(\mathbf{r}), \text{ with } I = 1, \dots, N_S \quad (4)$$

with the effective subsystem potential given by

$$v_{\text{eff}}^I(\mathbf{r}) = \underbrace{v_{\text{ext}}(\mathbf{r}) + v_{\text{eN}}^I(\mathbf{r}) + v_{\text{Coul}}^I(\mathbf{r}) + v_{\text{xc}}^I(\mathbf{r})}_{\text{same as regular KS-DFT}} + v_{\text{emb}}^I(\mathbf{r}). \quad (5)$$

In the above it is clear that if an external potential is applied to the system, v_{ext} , every subsystem will experience the same potential. In the so-called Frozen Density Embedding (FDE) formulation of subsystem DFT [12, 38], the unknown potential above, v_{emb} , is called embedding potential and is

given by

$$v_{\text{emb}}^I(\mathbf{r}) = \sum_{J \neq I} \left[\int \frac{\rho_J(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \sum_{\alpha \in J} \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} \right] + \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} - \frac{\delta T_s[\rho_I]}{\delta \rho_I(\mathbf{r})} + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})} - \frac{\delta E_{\text{xc}}[\rho_I]}{\delta \rho_I(\mathbf{r})}. \quad (6)$$

Throughout this work, “subsystem DFT” is used as a synonym of FDE. The density of the supersystem is thus given by $\rho(\mathbf{r}) = 2 \sum_I^{N_S} \sum_i^{\text{occ}_I} |\phi_i^I(\mathbf{r})|^2$.

2.2 Linear response TD-DFT

The time-dependent KS equation,

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}, t) \right] \phi_k(\mathbf{r}, t) = i \frac{\partial \phi_k(\mathbf{r}, t)}{\partial t}, \quad (7)$$

relates the time dependent KS orbitals, $\phi_k(\mathbf{r}, t)$, and the correlated density, $\rho(\mathbf{r}, t) = 2 \sum_k^{\text{occ}} |\phi_k(\mathbf{r}, t)|^2$, with the external perturbation $v_{\text{ext}}(\mathbf{r}, t)$. When starting from the ground state density, the time-dependent KS potential is defined according to Eq.(2) as

$$v_{\text{eff}}(\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + v_{\text{eN}}(\mathbf{r}) + v_{\text{Coul}}(\mathbf{r}, t) + v_{\text{xc}}(\mathbf{r}, t), \quad (8)$$

The external time-dependent potential in Eq.(8) is often referred to as “applied” potential [31,39] and it constitutes the only time-dependent perturbation causing the density ρ to become a time-dependent function. With the exception of v_{eN} , which is considered static (the nuclei are assumed to be still in the time the perturbation is applied), the other potential terms part of the effective KS potential are dependent on time, but only as a result of the perturbation $v_{\text{ext}}(\mathbf{r}, t)$.

Linear-response TD-DFT is based on the assumption that the density response to the external weak perturbation is given by the following linear-

response integral equations [40]

$$\delta\rho(\mathbf{r}, t) = \int d\mathbf{r}' \chi(\mathbf{r}, t, \mathbf{r}', t') \delta v_{\text{ext}}(\mathbf{r}', t') d\mathbf{r}' dt' \quad (9)$$

$$= \int d\mathbf{r}' \chi^0(\mathbf{r}, t, \mathbf{r}', t') \delta v_{\text{eff}}(\mathbf{r}', t') d\mathbf{r}' dt', \quad (10)$$

where

$$\delta v_{\text{eff}}(\mathbf{r}', t) = \delta v_{\text{ext}}(\mathbf{r}', t) + \delta v_{\text{ind}}(\mathbf{r}', t), \quad (11)$$

The induced potential, δv_{ind} , is expressed in linear response as well, namely

$$\delta v_{\text{ind}}(\mathbf{r}', t) = \int_{t'=t_0}^{t'=t} \int \left[\frac{\delta(t-t')}{|\mathbf{r}' - \mathbf{r}''|} + \frac{\delta v_{\text{xc}}(\mathbf{r}', t)}{\delta\rho(\mathbf{r}'', t')} \right] \delta\rho(\mathbf{r}'', t') d\mathbf{r}'' dt'. \quad (12)$$

The quantity $\frac{\delta v_{\text{xc}}(\mathbf{r}', t)}{\delta\rho(\mathbf{r}'', t')}$ is called the XC kernel, $f_{\text{xc}}(\mathbf{r}', t, \mathbf{r}'', t')$. The functions $\chi(\mathbf{r}, t, \mathbf{r}', t')$ and $\chi^0(\mathbf{r}, t, \mathbf{r}', t')$ are the correlated and the simplified KS response functions (or simply “correlated response” and “KS response”, respectively). Eq.(9) constitutes the definition of linear-response TD-DFT, and Eq.(10) derives from Eq.(9) from the Runge–Gross theorem (Theorem 4 of Ref. [41]). In the rest of this work, retardation effects are neglected and the adiabatic approximation is assumed, i.e. $f_{\text{xc}}(\mathbf{r}, t, \mathbf{r}', t') = f_{\text{xc}}(\mathbf{r}, \mathbf{r}')\delta(t-t')$, $\chi^0(\mathbf{r}, t, \mathbf{r}', t') = \chi^0(\mathbf{r}, \mathbf{r}')\delta(t-t')$. In addition, $\delta v_{\text{ext}}(\mathbf{r}, t) = \delta v_{\text{ext}}(\mathbf{r})$ in the linear response integral equations, and thus the XC kernel is assumed to be exactly the functional derivative of the XC potential [42].

For practical calculations, Eq.(10) is the most important. This is because, in the adiabatic approximation it involves quantities that can be easily extracted from the ground state KS system, such as the KS response function (given here in Fourier transform)

$$\chi^0(\mathbf{r}, \mathbf{r}', \omega) = \sum_i^{\text{occ}} \sum_a^{\text{virt}} \frac{2\omega_{ia}}{\omega_{ia}^2 - \omega^2} \phi_i(\mathbf{r}) \phi_a(\mathbf{r}) \phi_i(\mathbf{r}') \phi_a(\mathbf{r}'), \quad (13)$$

where ϕ_i and ϕ_a are occupied and virtual KS orbitals. In a simpler notation, omitting the integral signs and the variable dependence, practical calculation of the density response are carried out by self-consistently solving the following [40]

$$\left[(\chi^0)^{-1} - f \right] \delta\rho = \delta v_{\text{ext}}, \quad (14)$$

with

$$f(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}'). \quad (15)$$

As Eq.(14) must hold for any δv_{ext} , comparison with Eq.(9) yields

$$(\chi)^{-1} = (\chi^0)^{-1} - f, \quad (16)$$

also known as the Dyson equation for the response function [40, 42, 43].

3 Subsystem TD-DFT

This section is devoted to the derivation of linear response subsystem TD-DFT. Even though this theory has been first derived by Neugebauer [32], here it is presented in a different mathematical formalism. The derivations and analyses presented in this section are important as they pave the road to the formalism presented the subsequent sections.

3.1 Mathematical derivation

Following the usual decomposition of the density change in subststem TD-DFT [20, 25, 32], the total electron density change of the system, $\delta\rho$, due to an external perturbation is given exactly by

$$\delta\rho(\mathbf{r}, t) = \sum_I^{N_S} \delta\rho_I(\mathbf{r}, t), \quad (17)$$

where $\delta\rho_I$ is the density change of the single subsystem I . Similarly to Eq.(11), consider the effective time-dependent perturbation on subsystem I , $\delta v_{\text{eff}}^I(\mathbf{r}, t)$, being a functional of all the subsystem densities, and defined as follows

$$\delta v_{\text{eff}}^I(\mathbf{r}, t) = \underbrace{\delta v_{\text{ext}}(\mathbf{r}, t)}_{\text{perturbation}} + \underbrace{\delta v_{\text{ind}}^I(\mathbf{r}, t)}_{\substack{\text{induced potential} \\ \text{on subsystem I}}} \quad . \quad (18)$$

Similarly to Eq.(5), in the above it is assumed that the external potential is applied to the entire system and therefore it is the same external potential, δv_{ext} , that interacts with all the subsystems. The induced potential, δv_{ind}^I , can be defined in terms of the following functional derivatives of the subsystem KS potential given in Eq.(5) [20]

$$\delta v_{\text{ind}}^I(\mathbf{r}, t) = \sum_J^{N_S} \int \frac{\delta v_{\text{ind}}^I(\mathbf{r})}{\delta \rho_J(\mathbf{r}')} \delta \rho_J(\mathbf{r}', t) d\mathbf{r}' \quad (19)$$

$$\frac{\delta v_{\text{ind}}^I(\mathbf{r})}{\delta \rho_J(\mathbf{r}')} = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}[\rho](\mathbf{r}, \mathbf{r}') + \frac{\delta^2 T_s[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} - \frac{\delta^2 T_s[\rho_I]}{\delta \rho_I(\mathbf{r}) \delta \rho_J(\mathbf{r}')} \delta_{IJ}. \quad (20)$$

Following the adiabatic approximation, in the above equation the definition of XC kernel, f_{xc} , from Eq.(12) has been used and the time-dependence of the various kernels (kinetic and XC) has been neglected. Similarly to Eq.(9) and Eq.(10), with the aid of the Runge-Gross theorem, the time-dependent subsystem density can be obtained self consistently as

$$\delta \rho_I(\mathbf{r}, t) = \int \chi_I^c(\mathbf{r}, \mathbf{r}', t) \delta v_{\text{ext}}^I(\mathbf{r}') d\mathbf{r}' \quad (21)$$

$$= \int \chi_I^0(\mathbf{r}, \mathbf{r}', t) \delta v_{\text{eff}}^I(\mathbf{r}') d\mathbf{r}', \quad (22)$$

where χ_I^0 is the KS response of the subsystem to the external perturbation, χ_I^c is the correlated “coupled” subsystem response function, and δv_{eff}^I is given by Eqs.(18–19).

The above equations hold a great deal of information, e.g. the subsystem time-dependent density can be obtained from the simplified subsystem KS response function and the effective time-dependent potential. Eqs.(18–19) can be used in Eq.(22), yielding

$$\begin{aligned}\delta\rho_I(\mathbf{r}, t) = & \int \chi_I^0(\mathbf{r}, \mathbf{r}', t) \delta v_{\text{ext}}(\mathbf{r}') d\mathbf{r}' + \\ & \int \chi_I^0(\mathbf{r}, \mathbf{r}', t) \sum_J \frac{\delta v_{\text{ind}}^I(\mathbf{r}')}{\delta\rho_J(\mathbf{r}'')} \delta\rho_J(\mathbf{r}'', t) d\mathbf{r}' d\mathbf{r}'',\end{aligned}\quad (23)$$

and by grouping the terms involving $\delta\rho_I$ on the lhs and expressing $\delta\rho_I(\mathbf{r}, t)$ in terms of integrals of suitable Dirac deltas

$$\begin{aligned}& \int \left[\delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}'') - \chi_I^0(\mathbf{r}, \mathbf{r}', t) \frac{\delta v_{\text{ind}}^I(\mathbf{r}')}{\delta\rho_I(\mathbf{r}'')} \right] \delta\rho_I(\mathbf{r}'', t) d\mathbf{r}' d\mathbf{r}'' = \\ & = \int \chi_I^0(\mathbf{r}, \mathbf{r}', t) \delta v_{\text{ext}}(\mathbf{r}') d\mathbf{r}' + \int \chi_I^0(\mathbf{r}, \mathbf{r}', t) \sum_{J \neq I} \frac{\delta v_{\text{ind}}^I(\mathbf{r}')}{\delta\rho_J(\mathbf{r}'')} \delta\rho_J(\mathbf{r}'', t) d\mathbf{r}' d\mathbf{r}''.\end{aligned}\quad (24)$$

Eq.(24) can be rearranged by acting on the left by $(\chi_I^0)^{-1}(\mathbf{r}''', \mathbf{r}, t)$ and integrating over $d\mathbf{r}$, using the relation $\int (\chi_I^0)^{-1}(\mathbf{r}''', \mathbf{r}, t) \chi_I^0(\mathbf{r}, \mathbf{r}', t) d\mathbf{r} = \delta(\mathbf{r}''' - \mathbf{r}')$,

$$\begin{aligned}& \int \left[(\chi_I^0)^{-1}(\mathbf{r}''', \mathbf{r}', t) \delta(\mathbf{r}' - \mathbf{r}'') - \delta(\mathbf{r}''' - \mathbf{r}') \frac{\delta v_{\text{ind}}^I(\mathbf{r}')}{\delta\rho_I(\mathbf{r}'')} \right] \delta\rho_I(\mathbf{r}'', t) d\mathbf{r}' d\mathbf{r}'' = \\ & = \delta v_{\text{ext}}(\mathbf{r}''') + \int \delta(\mathbf{r}''' - \mathbf{r}') \sum_{J \neq I} \frac{\delta v_{\text{ind}}^I(\mathbf{r}')}{\delta\rho_J(\mathbf{r}'')} \delta\rho_J(\mathbf{r}'', t) d\mathbf{r}' d\mathbf{r}''.\end{aligned}\quad (25)$$

After integration over \mathbf{r}' and substitution of $\mathbf{r}''' \rightarrow \mathbf{r}$ and $\mathbf{r}'' \rightarrow \mathbf{r}'$ the following is obtained

$$\int \left[(\chi_I^0)^{-1}(\mathbf{r}, \mathbf{r}', t) - \frac{\delta v_{\text{ind}}^I(\mathbf{r})}{\delta\rho_I(\mathbf{r}')} \right] \delta\rho_I(\mathbf{r}', t) d\mathbf{r}' = \delta v_{\text{ext}}(\mathbf{r}) + \int \sum_{J \neq I} \frac{\delta v_{\text{ind}}^I(\mathbf{r})}{\delta\rho_J(\mathbf{r}')} \delta\rho_J(\mathbf{r}', t) d\mathbf{r}'.\quad (26)$$

Substitution of

$$K_{IJ}(\mathbf{r}, \mathbf{r}') = \frac{\delta v_{\text{ind}}^I(\mathbf{r})}{\delta \rho_J(\mathbf{r}')}, \quad (27)$$

allows for the definition of the “uncoupled” subsystem response function as

$$(\chi_I^u)^{-1}(\mathbf{r}, \mathbf{r}', t) = (\chi_I^0)^{-1}(\mathbf{r}, \mathbf{r}', t) - K_{II}(\mathbf{r}, \mathbf{r}'). \quad (28)$$

Realizing that Eq.(26) holds for **every** subsystem, the following $N_S \times N_S$ matrix vector equation can be formally constructed

$$\mathbf{M} \delta \boldsymbol{\rho} = \mathbf{1} \delta v_{\text{ext}}, \quad (29)$$

with

$$\mathbf{M} = \begin{pmatrix} (\chi_I^u)^{-1} & & -\mathbf{K} \\ & \ddots & \\ -\mathbf{K} & & (\chi_{N_S}^u)^{-1} \end{pmatrix}, \quad (30)$$

and

$$\delta \boldsymbol{\rho} = \begin{pmatrix} \delta \rho_I \\ \vdots \\ \delta \rho_{N_S} \end{pmatrix}, \quad (31)$$

where \mathbf{K} is the matrix composed of the K_{IJ} kernels. If the matrix in Eq.(30) is invertible, then the poles of \mathbf{M}^{-1} occur at the true excitation energies of each subsystem, and hence of the total supersystem. Eq.(29) can be considered the subsystem DFT equivalent of Eq.(14). The matrix formulation above yields the coupled subsystem response function defined in Eq.(22) as

$$\delta \rho_I = (\mathbf{M}^{-1})_{II} \delta v_{\text{ext}}, \quad (32)$$

thus a formal relationship is

$$\chi_I^c = (\mathbf{M}^{-1})_{II}, \quad (33)$$

and

$$\delta\rho = \text{Tr} [\mathbf{M}^{-1}] \delta v_{\text{ext}}. \quad (34)$$

Equations (32–34) are well suited to be used in practical calculations. This is because, in practice, all the operators (response functions and kernels) are expressed in a matrix form. The next section is devoted to the exploration of practical schemes for the solutions of Eqs.(29–34).

3.2 Practical calculations

In the occupied (i, j, \dots) and virtual (a, b, \dots) KS orbital basis set, the supermatrix \mathbf{K} occurring in Eq.(30) is defined as

$$\mathbf{K}_{(ia)_I(jb)_J} = \int \phi_{i_I}(\mathbf{r}) \phi_{a_I}(\mathbf{r}) \left(\frac{\delta v_I(\mathbf{r})}{\delta \rho_J(\mathbf{r}')} \right) \phi_{j_J}(\mathbf{r}') \phi_{b_J}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \quad (35)$$

With that, the orbital rotation Hessians can also be defined in a finite basis

$$(\mathbf{A} - \mathbf{B})_{(ia)_I(jb)_J} = (\epsilon_a^I - \epsilon_i^I) \delta_{ij} \delta_{ab} \delta_{IJ}, \quad (36)$$

$$(\mathbf{A} + \mathbf{B})_{(ia)_I(jb)_J} = (\epsilon_a^I - \epsilon_i^I) \delta_{ij} \delta_{ab} \delta_{IJ} + 2\mathbf{K}_{(ia)_I(jb)_J}. \quad (37)$$

If \mathbf{X} and \mathbf{Y} are vectors associated with the usual excitation and de-excitation components of the transition density matrix [44,45], solutions of the following anti-hermitian eigenvalue problem [28] corresponds to setting $\delta v_{\text{ext}} = 0$ and is equivalent to inverting the matrix in Eq.(30), for only two subsystems using Eq.(29) yields

$$\mathbf{M}\delta\rho = \left[\begin{pmatrix} \Lambda_I & \mathbf{K}_{IJ} \\ \mathbf{K}_{JI} & \Lambda_J \end{pmatrix} - \omega \begin{pmatrix} \Delta_I & \mathbf{0} \\ \mathbf{0} & \Delta_J \end{pmatrix} \right] \begin{pmatrix} \delta\rho_I \\ \delta\rho_J \end{pmatrix} = \mathbf{0}, \quad (38)$$

where, in the finite basis, $\delta\rho_I = \begin{pmatrix} \mathbf{X}_I \\ \mathbf{Y}_I \end{pmatrix}$, $\Lambda_I = \begin{pmatrix} \mathbf{A}_I & \mathbf{B}_I \\ \mathbf{B}_I & \mathbf{A}_I \end{pmatrix}$, and Δ_I are the matrices with zero off-diagonal element and 1 in the diagonal elements corresponding to \mathbf{X}_I and -1 for the ones corresponding to \mathbf{Y}_I . A perturbative approximation to Eq.(33) is [25, 32]

$$\left([\Lambda_I - \omega\Delta_I] - \sum_{J \neq I}^{N_S} \mathbf{K}_{IJ} [\Lambda_J - \omega\Delta_J]^{-1} \mathbf{K}_{JI} \right) \delta\rho_I = \mathbf{0}. \quad (39)$$

The matrix representation of the subsystem response function in the uncoupled formalism is defined as

$$\chi_I^u = [\Lambda_I - \omega\Delta_I]^{-1}. \quad (40)$$

Applying Eq.(39) iteratively yields the subsystem coupled response (χ_I^c) as defined in Eq.(33). If, instead, it is applied only once, it yields a perturbative subsystem coupled response function

$$(\chi_{I,\text{pert}}^c)^{-1} = (\chi_I^u)^{-1} - \sum_{J \neq I}^{N_S} \mathbf{K}_{IJ} \chi_J^u \mathbf{K}_{JI}. \quad (41)$$

The use of Eq.(40) and iteratively of Eq.(39) [or equivalently Eq.(41)] for the solution of uncoupled and coupled subsystem TD-DFT, respectively, has shown great success for the calculation of excitation energies, as well as for such molecular properties notoriously affected by the environmental response, such as circular dichroism and excitonic couplings [20, 25, 27, 28, 32, 33, 46].

Several remarks should be made about the above formalism. In the degenerate case, for example when dimers are considered, the above equation runs into numerical inaccuracies. That is because of the occurrence of poles in the uncoupled response at exactly the same frequencies as the zeroes of the inverse uncoupled response. In those cases, Neugebauer has circumvented the

problem [32] by abandoning the effective perturbative treatment above and by directly inverting the part of the \mathbf{M} matrix corresponding to the subspace spanned by the two monomers. In a second step, Eq.(41) can be applied to account for the coupling with all the remainder subsystems. In the degenerate case, the coupled subsystem response function is not given by Eq.(39) but instead takes a more complicated form, given implicitly by Eq.(34). It is, therefore, concluded that Eq.(41) can be considered a perturbative solution [47] and thus it does not represent the true coupled subsystem response function.

In the following section, an alternative derivation of subsystem TD-DFT is carried out. The new derivation is such that: (1) the coupled response is defined explicitly even in the degenerate case, and (2) it is consistent with and recovers the original formulation.

4 Alternative Derivation of Susbsystem TD-DFT

4.1 Mathematical derivation

Eq.(26) can be rearranged as follows,

$$\begin{aligned} & \int (\chi_I^u)^{-1}(\mathbf{r}, \mathbf{r}', t) \chi_I^c(\mathbf{r}', \mathbf{r}'', t) \delta v_{\text{ext}}(\mathbf{r}'') d\mathbf{r}'' d\mathbf{r}' = \\ & = \int \left[\delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}'') + \sum_{J \neq I} K_{IJ}(\mathbf{r}, \mathbf{r}') \chi_J^c(\mathbf{r}', \mathbf{r}'', t) \right] \delta v_{\text{ext}}(\mathbf{r}'') d\mathbf{r}'' d\mathbf{r}'. \quad (42) \end{aligned}$$

The above equation must hold for any $\delta v_{\text{ext}}(\mathbf{r}'')$, and specifically for $\delta v_{\text{ext}}(\mathbf{r}'') = \delta(\mathbf{r}'' - \tilde{\mathbf{r}})$. Integration over $d\mathbf{r}''$ yields

$$\int (\chi_I^u)^{-1}(\mathbf{r}, \mathbf{r}', t) \chi_I^c(\mathbf{r}', \tilde{\mathbf{r}}, t) d\mathbf{r}' = \delta(\mathbf{r} - \tilde{\mathbf{r}}) + \int \sum_{J \neq I} K_{IJ}(\mathbf{r}, \mathbf{r}') \chi_J^c(\mathbf{r}', \tilde{\mathbf{r}}, t) d\mathbf{r}'. \quad (43)$$

Thus, after applying $\chi_I^u(\mathbf{r}'', \mathbf{r}, t)$ and integration over $d\mathbf{r}$, the following Dyson-type equation is obtained, in simplified notation,

$$\chi_I^c = \chi_I^u + \sum_{J \neq I}^{N_S} \chi_I^u K_{IJ} \chi_J^c. \quad (44)$$

The main difference between the above Dyson equation and the one in Eq.(41) is that the former should be considered a more general Dyson equation, as it is derived in the general case without assuming a finite basis expansion of the involved operators. In addition, it does not employ a perturbative approach.

Dyson equations for the response functions involving only the kernels and the KS response functions are derived starting from Eq.(26) and read as follows

$$\chi_I^u = \chi_I^0 + \chi_I^0 K_{II} \chi_I^u, \quad (45)$$

$$\chi_I^c = \chi_I^0 + \chi_I^0 \sum_J^{N_S} K_{IJ} \chi_J^c. \quad (46)$$

Similarly to regular TD-DFT, this formulation shows that the uncoupled response in Eq.(45) is similar to the one of the isolated subsystem, with a small correction in the kernel due to the second functional derivative of the kinetic energy. In addition, the coupling between subsystem responses in Eq.(46) is mediated by the off-diagonal elements of the kernel matrix \mathbf{K} .

In sharp contrast to the original formalism, here it is evident that if the

poles of the response function of subsystem I are well separated from the ones of the other subsystem response functions, then the poles of each subsystem response contain the ones of all other subsystems. This is a particularly interesting result, as it shows that formally the correlated response function of a single subsystem contains information about the electronic spectrum of the entire supersystem. Obviously, in the limit of infinitely separated subsystems, $K_{IJ}(\mathbf{r}, \mathbf{r}')$ will be identically zero when \mathbf{r} and \mathbf{r}' span regions of space occupied by different subsystems. Thus, the above observation needs to be taken with a grain of salt as it is valid only if the subsystems are relatively close to each other.

Another interesting outcome of this formalism is that when two subsystems have poles at the same frequencies in the isolated case (or in the uncoupled case), then this degeneracy must disappear in the coupled case otherwise the response function would feature an unphysical “double pole”. This implies that the above formalism is coherent with the existence of Davydoff splittings in dimeric systems [32, 48].

4.2 Practical calculations

Even though Eq.(44) is aesthetically pleasing, it is not suitable for practical calculations. The perturbative solution in Eq.(29) is recovered by rewriting the above equation in matrix form. In the first step, let us rewrite Eq.(44) as

$$\chi_I^u = \chi_I^u \left[(\chi_I^u)^{-1} \chi_I^c - \sum_{J \neq I}^{N_S} K_{IJ} \chi_J^c \right]. \quad (47)$$

In the second step, the above equation is written in a more convenient matrix form

$$1 = \mathbf{M} \boldsymbol{\chi}^c, \quad (48)$$

where

$$\mathbf{M} = \begin{pmatrix} (\chi_I^u)^{-1} & & -\mathbf{K} \\ & \ddots & \\ -\mathbf{K} & & (\chi_{N_S}^u)^{-1} \end{pmatrix}, \quad (49)$$

is the same matrix defined in Eq.(30). Similarly as before, from Eq.(48), the poles of \mathbf{M}^{-1} are also the poles of the coupled response function. With this, the above matrix inversion can be approximated by a perturbative approach similarly to what is done in Eq.(41).

5 Comparison to TD-DFT of the supersystem

Comparison of subsystem DFT with regular KS-DFT is straightforward. In subsystem DFT one has to solve coupled KS-like equations, where the coupling term is conveniently expressed as a potential term, v_{emb} , added to the KS effective potential of the isolated subsystem. This means that the two formalisms involve similar algorithms for practical calculations.

As it will be clear from the following derivations, this is not the case for the time-dependent extensions. In the following, Dyson-type equations will make it possible to directly compare subsystem DFT with the TD-DFT of the supersystem. The correlated response of the supersystem has a simple relationship to the subsystem correlated responses, taking the functional derivative with respect to δv_{ext} of both sides of Eq.(17) one obtains

$$\chi = \sum_I^{N_S} \chi_I. \quad (50)$$

Conversely, due to the non-uniqueness of the density partitioning in Eq.(3), the “simplified” KS response of the supersystem has no simple relationship

with the subsystem KS responses.

5.1 Subsystem versus full KS response function

In order to find a relationship between the subsystem and the supersystem KS response functions, let us manipulate Eq.(21) by inverting the subsystem response functions, one by one, in the following manner

$$(\chi_I^0)^{-1} \delta\rho_I = \delta v_{\text{eff}}^I, \quad (51)$$

where we have omitted the integration symbols for sake of a lighter notation. An important difference between the induced potential used in subsystem TD-DFT defined in Eq.(20) and the one used in the TD-DFT of the supersystem defined in Eq.(12) resides in the kinetic energy kernels. The two can be related,

$$\delta v_{\text{eff}}^I(\mathbf{r}, t) = \delta v_{\text{eff}}(\mathbf{r}, t) + \delta v_{\text{T}}^I(\mathbf{r}, t), \quad (52)$$

where, using Eq.(19) and Eq.(20), we define the kinetic energy part of the subsystem kernel as

$$\begin{aligned} \delta v_{\text{T}}^I(\mathbf{r}, t) &= \sum_J^{N_S} \int \left(\frac{\delta^2 T_s[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} - \frac{\delta^2 T_s[\rho_I]}{\delta\rho_I(\mathbf{r})\delta\rho_J(\mathbf{r}')} \right) \delta\rho_J(\mathbf{r}', t) d\mathbf{r}' \\ &= \int f_{\text{T}}(\mathbf{r}, \mathbf{r}') \delta\rho(\mathbf{r}', t) - \int f_{\text{T}}^I(\mathbf{r}, \mathbf{r}') \delta\rho_I(\mathbf{r}', t), \end{aligned} \quad (53)$$

where Eq.(17) has been used for the first term of the rhs. Using Eq.(53) in Eq.(51), we obtain

$$\left[(\chi_I^0)^{-1} + f_{\text{T}}^I \right] \delta\rho_I = (1 + f_{\text{T}}\chi^0) \delta v_{\text{eff}}, \quad (54)$$

where the number 1 above is intended to be the identity in functional space, i.e. a Dirac delta in the position representation. Inverting the operator on the

lhs of the above equation and summing over all the subsystems, we obtain the following

$$\sum_I^{N_S} \delta \rho_I = \sum_I^{N_S} \left\{ \left[(\chi_I^0)^{-1} + f_T^I \right]^{-1} (1 + f_T \chi^0) \right\} \delta v_{\text{eff}}. \quad (55)$$

At this point there are several algebraically non-equivalent ways to proceed. Two routes are considered here: the first one leading to an exact expression, and the second one leading to expressions suited for approximations. Section 5.2 is devoted to an analysis of the following derivations.

5.1.1 Exact expression

Extracting χ^0 from the braces of Eq. (55), and realizing that $\chi^0 \delta v_{\text{eff}} = \delta \rho$

$$\delta \rho = \sum_I^{N_S} \left\{ \left[(\chi_I^0)^{-1} + f_T^I \right]^{-1} \left[(\chi^0)^{-1} + f_T \right] \right\} \chi^0 \delta v_{\text{eff}}. \quad (56)$$

By defining $(\chi_I^T)^{-1} = \left[(\chi_I^0)^{-1} + f_T^I \right]$, Eq. (56) leads to

$$\chi^0 = \left[\sum_I^{N_S} (\chi_I^T)^{-1} \right]^{-1} - f_T. \quad (57)$$

An important remark is that the KS supersystem considered here is the true KS supersystem. Other formulations of subsystem TD-DFT [31], instead, considered a supersystem defined similarly to KS-DFT, but solved with a modified potential containing the KS potential plus the total kinetic energy potential, $\frac{\delta T_s}{\delta \rho(\mathbf{r})}$.

5.1.2 Approximate expressions

A first approximation can be reached directly from Eq.(57) in the limit of vanishing kernels, namely

$$(\chi^0)^{-1} = \sum_I^{N_S} (\chi_I^0)^{-1}. \quad (58)$$

However, a different approximation can be made by first taking the functional derivative with respect to δv_{eff} on both sides of Eq.(55), namely

$$\chi^0 = \sum_I^{N_S} \chi_I^0 [1 + f_T^I \chi_I^0]^{-1} (1 + f_T \chi^0), \quad (59)$$

which can be arranged to

$$\chi^0 = [1 - f_T S]^{-1} S, \quad (60)$$

with $S = \sum_I^{N_S} \chi_I^0 [1 + f_T^I \chi_I^0]^{-1}$. The above inverse operations expression can be approximated with linear expansions, in the limit of small $f_T^I \chi_I^0$ and small $f_T \chi^0$, to

$$\chi^0 \simeq \sum_I^{N_S} \chi_I^0 - \sum_I^{N_S} \chi_I^0 f_T^I \chi_I^0 + \sum_{IJ}^{N_S} \chi_I^0 f_T \chi_J^0, \quad (61)$$

featuring an interesting resemblance to the Dyson equation for the response function.

It is instructive to notice how the supersystem KS response function calculated with the linear expansion of the inverse operations in Eq.(61) and neglecting the kinetic and exchange-correlation kernels, which we term here Random Phase Approximation (RPA), is exactly the sum of the subsystem response functions, i.e.

$$\chi^{0,\text{RPA}} = \sum_I^{N_S} \chi_I^{0,\text{RPA}}. \quad (62)$$

Assessing the performance of the RPA approximation compared to the exact expression in Eq.(57) and the approximation in Eq.(58) lies beyond the scope of this theoretical work and will be the focus of a future work.

5.2 Physical meaning of the subsystem KS responses and comparison to PDFT

The derivations in the preceding section stand out as being too complicated for just the KS response, paradoxically in this context known as the “simplified” response. What is the significance of such a complicated relationship between the supersystem and the subsystem KS response functions? What is puzzling in Eqs.(57–61) is that the KS response of the supersystem contains terms coupling the subsystem KS responses. This is not a very good property of this theory, as subsystem additivity is sought in the density, in the correlated response in Eq.(50) and it is expected to appear in the KS density response as well.

This apparent artifact is due to the non-uniqueness and subjectivity of the density partitioning employed in Eq.(3). An indication of this artificial behavior of the subsystem KS responses can be easily shown by considering a more refined version of subsystem DFT known as partition DFT (PDFT). In PDFT theory [49–52] the effective subsystem time-dependent potential is

$$\delta v_{\text{eff}}^I = \delta v_{\text{ext}} + \delta v_{\text{ind}} + \delta v_{\text{p}}, \quad (63)$$

where δv_{p} is the change in the partition potential (a quantity shared by all subsystems and thus **unique**). The above equation can be rearranged similarly to the step carried out between Eq.(54) and Eq.(55), to yield

$$\left[(\chi_I^0)^{-1} - f_{\text{p}} \right] \delta \rho_I = (\chi^0)^{-1} \delta \rho, \quad (64)$$

with $f_p = \frac{\delta v_p}{\delta \rho}$. The above equation is rearranged to

$$\chi^0 = \sum_I^{N_S} \left[(\chi_I^0)^{-1} - f_p \right]^{-1} \quad (65)$$

which can be approximated assuming small $f_p \chi_I^0$ by

$$\chi^0 \simeq \sum_I^{N_S} \chi_I^0 - \sum_I^{N_S} \chi_I^0 f_p^I \chi_I^0. \quad (66)$$

The last two equations feature no cross terms coupling the subsystem KS responses. Thus, PDFT provides a more intuitive time-dependent behavior of the subsystems and is completely free of artifacts due to the non-unique partitioning appearing in regular subsystem DFT.

Non-orthogonality also plays a role. For example, the simple relationship recovered in the RPA approximation in Eq.(62) is expected to hold more strongly in the limit of small electron density overlap between subsystems, i.e. quasi orthogonality, as the non-additive functionals in that case are close to being identically zero.

Another important remark is that Eqs.(57–61) establish a map between KS and FDE orbitals without having to invert the KS equation as it is done in recent works [53,54]. In principle, Eq.(61) can be used to approximate the KS orbitals by correcting to first order the subsystem orbitals. Developing the working equations for such a mapping is not in the scopes of this work and will be the subject of future studies.

6 Conclusions

In this work, the theory of linear-response subsystem TD-DFT is analyzed in detail. Two formulations are considered, one is equivalent to the theory presented by Neugebauer [25], and the other is presented in terms of Dyson

equations involving subsystem response functions. Three types of subsystem response functions are considered: coupled, uncoupled and KS response. The coupled and uncoupled are exact and approximated correlated subsystem responses, respectively.

It is found that, for non-infinitely separated subsystems, the pole structure of the correlated (coupled) subsystem response functions contains the excitations of the entire supersystem. This shows that if an external potential is in resonance with an electronic transition of one subsystem, the electronic response of another subsystem will also be strongly affected. This behaviour generally does not fit a picture of “localized excitations” [16] but instead is consistent with the idea that the response of a collection of subsystems is collective. Localization of the excitations may take place whenever the kernel coupling the subsystem’s excitations K_{IJ} is small.

Comparison of the subsystem responses with the response functions of the supersystem shows that, while the correlated response is subsystem additive, the KS response is not. This particularly puzzling aspect of the theory is found to be an artifact stemming from the subjective nature of the density partitioning, as it is not found in time-dependent PDFT theory.

This work sets the stage for a number of important theoretical advances, such as the development of quasiparticle GW corrections to subsystem DFT, and the setting up of a mapping between subsystem and supersystem KS orbitals through the expressions relating the KS response functions. The evaluation of non-local correlation energy, and thus the account of dispersion interactions between subsystems, is also a possible outcome of this theory and is being investigated as a future development.

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References

- [1] W. Kohn and L. J. Sham, Phys. Rev. **140**, 1133 (1965).
- [2] G. E. Scuseria, J. Phys. Chem. A **103**, 4782 (1999).
- [3] S. Goedecker, Rev. Mod. Phys. **71**, 1085 (1999).
- [4] D. R. Bowler and T. Miyazaki, Rep. Prog. Phys. **75**, 036503 (2012).
- [5] P. Carloni, U. Rothlisberger, and M. Parrinello, Acc. Chem. Res. **35**, 455 (2002).
- [6] K. Burke, J. Chem. Phys. **136**, 150901 (2012).
- [7] R. G. Gordon and Y. S. Kim, J. Chem. Phys. **56**, 3122 (1972).
- [8] Y. S. Kim and R. G. Gordon, J. Chem. Phys. **60**, 1842 (1974).
- [9] B. Jeziorski and W. Kołos, Perturbation approach to the study of weak intermolecular interactions, in *Molecular Interactions, Vol. 3*, edited by H. Ratajczak and W. J. Orville-Thomas, pages 1–46, Wiley, Chichester, 1982.
- [10] G. Senatore and K. R. Subbaswamy, Phys. Rev. B **34**, 5754 (1986).
- [11] P. Cortona, Phys. Rev. B **44**, 8454 (1991).
- [12] T. A. Wesolowski and A. Warshel, J. Phys. Chem. **97**, 8050 (1993).

- [13] P. de Silva and T. A. Wesolowski, *J. Chem. Phys.* **137**, 094110 (2012).
- [14] X. Hu, Y. Jin, X. Zeng, H. Hu, and W. Yang, *Phys. Chem. Chem. Phys.* **14**, 7700 (2012).
- [15] M. Pavanello, T. Van Voorhis, L. Visscher, and J. Neugebauer, *J. Chem. Phys.* (2013), Submitted, available at <http://arxiv.org/abs/1211.4880>.
- [16] A. S. P. Gomes and C. R. Jacob, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **108**, 222 (2012).
- [17] S. Höfener, A. S. P. Gomes, and L. Visscher, *J. Chem. Phys.* **136**, 044104 (2012).
- [18] S. Laricchia, E. Fabiano, and F. D. Sala, *J. Chem. Phys.* **137**, 014102 (2012).
- [19] J. D. Goodpaster, T. A. Barnes, and T. F. Miller, III, *J. Chem. Phys.* **134**, 164108 (2011).
- [20] J. Neugebauer, *Phys. Rep.* **489**, 1 (2010).
- [21] M. Iannuzzi, B. Kirchner, and J. Hutter, *Chem. Phys. Lett.* **421**, 16 (2006).
- [22] S. Fux, K. Kiewisch, C. R. Jacob, J. Neugebauer, and M. Reiher, *Chem. Phys. Lett.* **461**, 353 (2008).
- [23] A. Solovyeva, M. Pavanello, and J. Neugebauer, *J. Chem. Phys.* **136**, 194104 (2012).
- [24] M. Pavanello and J. Neugebauer, *J. Chem. Phys.* **135**, 234103 (2011).
- [25] J. Neugebauer, C. Curutchet, A. Munoz-Losa, and B. Mennucci, *J. Chem. Theory Comput.* **6**, 1843 (2010).

- [26] A. S. P. Pawel Tecmer, Henk van Lingen and L. Visscher, J. Chem. Phys. **137**, 084308 (2012).
- [27] C. König, N. Schlüter, and J. Neugebauer, J. Chem. Phys. (2012), Accepted.
- [28] C. König and J. Neugebauer, Phys. Chem. Chem. Phys. **13**, 10475 (2011).
- [29] R. E. Bulo, C. R. Jacob, and L. Visscher, J. Phys. Chem. A **112**, 2640 (2008).
- [30] C. R. Jacob and L. Visscher, J. Chem. Phys. **125**, 194104 (2006).
- [31] M. E. Casida and T. A. Wesolowski, Int. J. Quantum Chem. **96**, 577 (2004).
- [32] J. Neugebauer, J. Chem. Phys. **126**, 134116 (2007).
- [33] J. Neugebauer, J. Chem. Phys. **131**, 084104 (2009).
- [34] J. Neugebauer, M. J. Louwerse, E. J. Baerends, and T. A. Wesolowski, J. Chem. Phys. **122**, 094115 (2005).
- [35] F. Furche and T. Van Voorhis, J. Chem. Phys. **122**, 164106 (2005).
- [36] D. C. Langreth, M. Dion, H. Rydberg, E. Schröder, P. Hyldgaard, and B. I. Lundqvist, Int. J. Quantum Chem. **101**, 599 (2005).
- [37] F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61**, 237 (1998).
- [38] T. A. Wesolowski, One-electron Equations for Embedded Electron Density: Challenge for Theory and Practical Payoffs in Multi-Level Modeling of Complex Polyatomic Systems, in *Computational Chemistry: Reviews of Current Trends*, edited by J. Leszczynski, volume 10, pages 1–82, World Scientific, Singapore, 2006.

- [39] M. E. Casida and M. Huix-Rotllant, *Annu. Rev. Phys. Chem.* **63**, 287 (2012).
- [40] M. E. Casida, Time-Dependent Density Functional Response Theory for Molecules, in *Recent Advances in Density Functional Methods Part I*, edited by D. P. Chong, pages 155–192, World Scientific, Singapore, 1995.
- [41] E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984).
- [42] E. K. U. Gross, J. F. Dobson, and M. Petersilka, Density Functional Theory of Time-Dependent Phenomena, in *Density Functional Theory II*, edited by J. D. Dunitz, K. Hafner, K. N. Houk, S. Ito, J.-M. Lehn, K. N. Raymond, C. W. Rees, J. Thiem, and F. Vögtle, Topics in Current Chemistry, pages 81–172, Springer, 1996.
- [43] M. Petersilka, U. J. Gossmann, and E. K. U. Gross, *Phys. Rev. Lett.* **76**, 1212 (1996).
- [44] F. Furche, *J. Chem. Phys.* **114**, 5982 (2001).
- [45] A. Dreuw and M. Head-Gordon, *Chem. Rev.* **105**, 4009 (2005).
- [46] J. Neugebauer, *J. Phys. Chem. B* **112**, 2207 (2008).
- [47] R. McWeeny, *Methods of Molecular Quantum Mechanics*, Academic Press, San Diego, 1992.
- [48] A. S. Davydov, *Theory of Molecular Excitons*, McGraw-Hill, New York, 1962.
- [49] R. Tang, J. Nafziger, and A. Wasserman, *Phys. Chem. Chem. Phys.* **14**, 7780 (2012).

- [50] P. Elliott, K. Burke, M. H. Cohen, and A. Wasserman, Phys. Rev. A **82**, 024501 (2010).
- [51] M. H. Cohen, A. Wasserman, R. Car, and K. Burke, J. Phys. Chem. A **113**, 2183 (2009).
- [52] P. Elliott, M. H. Cohen, A. Wasserman, and K. Burke, J. Chem. Theory Comput. **5**, 827 (2009).
- [53] S. Fux, C. R. Jacob, J. Neugebauer, L. Visscher, and M. Reiher, J. Chem. Phys. **132**, 164101 (2010).
- [54] J. D. Goodpaster, N. Ananth, , F. R. Manby, and T. F. Miller, III, J. Chem. Phys. **133**, 084103 (2010).